

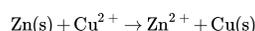
16.3: Cell Potentials and Thermodynamics

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- When we refer to the "standard potential of a half-cell" or "couple" M^{2+}/M , we mean the potential difference $E_{right} - E_{left}$ of the cell
- If the potential difference of this cell is positive ($E_{right} - E_{left} > 0$), electrons will flow through an external circuit from the Pt/H_2 electrode to the M electrode and the cell reaction will spontaneously proceed in the direction written. The more positive the cell potential, the greater the tendency of this reaction to occur and the stronger the oxidizing agent M^{2+} .
- Through the relation $E^\circ = -\Delta G^\circ/nF$ it is apparent that a standard half-cell reduction potential is simply the decrease in the free energy per mole of electrons transferred to H^+ ions under the conditions that define the SHE. Strong reducing agents (good electron donors) have more negative E° 's, while strong oxidizing agents (good acceptors) have more positive E° 's.
- For a more general cell $X(s) | X^+ || M^{2+} | M(s)$, E° is similarly the fall in free energy per electron-mole when M^{2+} is reduced by X . This reaction can proceed spontaneously only if the cell potential is positive (ΔG° negative.)
- An *electron free energy diagram* that displays various redox couples on a vertical scale of free energies relative to H^+ serves as a convenient means of visualizing the possible reactions when two or more redox-active pairs are present in a solution. The position of a redox couple in relation to those of the H_2/H^+ and $H_2O/O_2, H^+$ couples is especially significant because it indicates whether a given species will be thermodynamically stable in water.
- *Latimer diagrams* provide a convenient means of correlating the various oxidation states of a particular element.

It has long been known that some metals are more "active" than others in the sense that a more active metal can "displace" a less active one from a solution of its salt. The classic example is the one we have already mentioned on the preceding page:



Here zinc is more active because it can displace (precipitate) copper from solution. If you immerse a piece of metallic zinc in a solution of copper sulfate, the surface of the zinc quickly becomes covered with a black coating of finely-divided copper, and the blue color of the hydrated copper(II) ion diminishes. Similar comparisons of other metals made it possible to arrange them in the order of their increasing electron-donating (reducing) power. This sequence became known as the electromotive or activity series of the metals.

The most active (most strongly reducing) metals appear on top, and least active metals appear on the bottom. A more active metal (such as Zn) will donate electrons to the cation of a less active metal (Cu^{2+} , for example.) Notice the special role of hydrogen here; although H_2 does not have the physical properties of a metal, it is capable of being "displaced" (a rather archaic term seldom used in modern chemistry) from H_2O or H^+ -containing (acidic) solutions. Note that the "active" metals are all "attacked by acids"; what this really means is that they are capable of donating electrons to H^+ .

displace H_2 from water, steam, or acids	Li	$2 Li(s) + 2 H_2O(l) \rightarrow 2 LiOH(aq) + H_2(g)$
	K	$2 K(s) + 2 H_2O(l) \rightarrow 2 KOH(aq) + H_2(g)$
	Ca	$Ca(s) + 2 H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$
	Na	$2 Na(s) + 2 H_2O(l) \rightarrow 2 NaOH(aq) + H_2(g)$
displace H_2 from steam or acids	Mg	$Mg(s) + 2 H_2O(g) \rightarrow Mg(OH)_2(s) + H_2(g)$
	Al	$2 Al(s) + 6 H_2O(g) \rightarrow 2 Al(OH)_3(s) + 3 H_2(g)$
	Mn	$Mn(s) + 2 H_2O(g) \rightarrow Mn(OH)_2(s) + H_2(g)$
	Zn	$Zn(s) + 2 H_2O(g) \rightarrow Zn(OH)_2(s) + H_2(g)$
	Fe	$Fe(s) + 2 H_2O(g) \rightarrow Fe(OH)_2(s) + H_2(g)$
displace H_2 from acids only	Ni	$Ni(s) + 2 H^+(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$
	Sn	$Sn(s) + 2 H^+(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$
	Pb	$Pb(s) + 2 H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$
H_2		
can't displace H_2	Cu	
	Ag	
	Pt	
	Au	

The activity series has long been used to predict the direction of oxidation-reduction reactions. Consider, for example, the oxidation of Cu by metallic zinc that we have mentioned previously. The fact that zinc is near the top of the activity series means that this metal has a strong tendency to lose electrons. By the same token, the tendency of Zn to accept electrons is relatively small. Copper, on the other hand, is a poorer electron donor, and thus its oxidized form, Cu , is a fairly good electron acceptor. We would therefore expect the reaction



to proceed in the direction indicated, rather than in the reverse direction. An old-fashioned way of expressing this is to say that "zinc will displace copper from solution". The above table is of limited practical use because it does not take into account the concentrations of the dissolved species. In order to treat these reactions quantitatively, it is convenient to consider the oxidation and reduction steps separately.

Standard half-cell potentials

When a net reaction proceeds in an electrochemical cell, oxidation occurs at one electrode (the anode) and reduction takes place at the other electrode (the cathode.) We can think of the cell as consisting of two half-cells joined together by an external circuit through which electrons flow and an internal pathway that allows ions to migrate between them so as to preserve electroneutrality.

Reduction potentials

Each half-cell has associated with it an electrode-solution potential difference whose magnitude depends on the nature of the particular electrode reaction and on the concentrations of the dissolved electroactive species. The sign of this potential difference depends on the direction (oxidation or reduction) in which the electrode reaction proceeds. To express them in a uniform way, we adopt the convention that half-cell potentials are always defined for the reduction direction. Thus the half-cell potential for the Zn/Zn^{2+} electrode (or *couple* as it is sometimes called) always refers to the reduction reaction



In the cell $Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$ the zinc appears on the left side, indicating that it is being oxidized, not reduced. For this reason, the potential difference contributed by the left half-cell has the opposite sign to its conventional half-cell potential. More generally, we can define the cell potential (or cell EMF) as

$$E_{cell} = \Delta V = E_{right} - E_{left} \quad (16.3.3)$$

in which "right" and "left" refer to the cell notation convention ("reduction on the right") and not, of course, to the physical orientation of a real cell in the laboratory. If we expand the above expression we see that the cell potential

$$E_{cell} = V_{Cu} - V_{solution} + V_{solution} - V_{Zn} \quad (16.3.4)$$

is just the difference between the two half-cell potentials E_{right} and E_{left} .

Reference half-cells

The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. Although we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference half-cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

The reference cell that has universally been adopted for this purpose is the *hydrogen half-cell*



in which hydrogen gas is allowed to bubble over a platinum electrode having a specially treated surface which catalyzes the reaction

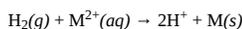


When this electrode is operated under standard conditions of 1 atm H_2 pressure, 25°C, and pH = 0, it becomes the standard hydrogen electrode, sometimes abbreviated SHE.

To measure the relative potential of some other electrode couple M^{2+}/M , we can set up a cell



whose net reaction is



the potential difference between the platinum and M electrodes will be

$$E_{cell} = V_M - V_{solution} + V_{solution} - V_{Pt}$$

but since the difference $V_{solution} - V_{Pt}$ is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to

$$E_{cell} = V_M - V_{solution}$$

which is just the potential (relative to that of the SHE) of the half-cell whose reaction is



Measurement of a standard reduction potential.

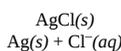
The M^{2+}/M half-cell is on the left, and the standard hydrogen cell is on the right. The two half-cells are joined through the salt bridge in the middle. The more "active" the metal M (the greater its tendency to donate electrons to H^+), the more negative will be $E_{cell} = \Delta V = E_{right} - E_{left}$

Standard [reduction] potentials are commonly denoted by the symbol E° . E° values for hundreds of electrodes have been determined (mostly in the period 1925-45, during which time they were referred to as "oxidation potentials") and are usually tabulated in order of increasing tendency to accept electrons (increasing oxidizing power.)

Table 2: some standard reduction potentials

oxidant (electron acceptor)	reductant (electron donor)	E° , volts
Na^+	$Na(s)$	-2.71
Zn^{2+}	$Zn(s)$	-.76
Fe^{2+}	$Fe(s)$	-.44
Cd^{2+}	$Cd(s)$	-.40
Pb^{2+}	$Pb(s)$	-.126

0.000



+ .222



	$2\text{Cl}^-(aq) + 2\text{Hg}(l)$
+0.268	
	Cu^{2+} $\text{Cu}(s)$
+0.337	
	$\text{I}_2(s)$ 2I^-
+0.535	
	Fe^{3+} Fe^{2+}
+0.771	
	Ag^+ $\text{Ag}(s)$
+0.799	
	$\text{O}_2(g) + 4\text{H}^+$ $2\text{H}_2\text{O}(l)$
+1.23	
	$\text{Cl}_2(g)$ 2Cl^-
+1.36	

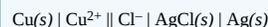
Note particularly that

- Unlike the activity series mentioned above, this table includes *non-metallic substances*, and it is *quantitative*.
- The more positive the half-cell EMF, the greater the tendency of the reductant to donate electrons, and the smaller the tendency of the oxidant to accept electrons.
- A species in the leftmost column can act as an oxidizing agent to any species above it in the reductant column.
- Oxidants such as Cl_2 that are below H_2O will tend to decompose water.

Given the E° values for two half reactions, you can easily predict the potential difference of the corresponding cell: simply add the reduction potential of the reduction half-cell to the *negative* of the reduction potential (that is, to the oxidation potential) of the oxidation reaction.

✓ Example 16.3.1

Find the standard potential of the cell



and predict the direction of electron flow when the two electrodes are connected.

Solution

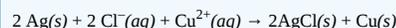
The net reaction corresponding to this cell will be:



Where $\text{Cu}(s)/\text{Cu}^{2+}$ is being Oxidized and $\text{Ag}(s)/\text{Ag}^+$ is being Reduced

$$E_{\text{cell}} = E_{\text{reduction}} + E_{\text{oxidation}} \text{ Or Written another way } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = (.222 + (-.337)) \text{ v} = \mathbf{-0.115 \text{ v}}$$

Since E_{cell} is negative, the reaction will run in the **opposite** direction. The correct net reaction will be:



Where $\text{Ag}(s)/\text{Ag}^+$ is being Oxidized and $\text{Cu}(s)/\text{Cu}^{2+}$ is being Reduced

$$E_{\text{cell}} = E_{\text{reduction}} + E_{\text{oxidation}} \text{ Or Written another way } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = (.337 + (-.222)) \text{ v} = \mathbf{+0.115 \text{ v}}$$

Since this potential is positive, the reaction will proceed to the right; electrons will be withdrawn from the silver electrode and flow through the external circuit into the copper electrode. Note carefully that in combining these half-cell potentials, we did not multiply E° for the Cu^{2+}/Cu couple by two. The reason for this will be explained later.

Cell potentials and Free (Gibbs) energy

From the above, it should be apparent that the potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus ΔG° and E° measure the same thing, and are related in a simple way:

$$\Delta G^\circ = -nFE^\circ \quad (16.3.9)$$

... or in more detail (see below for explanations of the units given for voltage)



A few remarks are in order about this very fundamental and important relation:

- The negative sign on the right indicates that a *positive cell potential* (according to the sign convention discussed previously) implies a *negative free energy change*, and thus that the cell reaction will spontaneously proceed to the *right*.
- Electrical work is done when an electric charge q moves through a potential difference ΔV . The right side of Eq. 2 refers to the movement of n moles of charge across the cell potential E° , and thus has the dimensions of *work*.

- The value of ΔG° expresses the maximum useful work that a system can do on the surroundings. "Useful" work is that which can be extracted from the cell by electrical means to operate a lamp or some other external device. This excludes any P - V work that is simply a consequence of volume change (which could conceivably be put to some use!) and which would be performed in any case, even if the reactants were combined directly. This quantity of work $-\Delta G^\circ$ can only be extracted from the system under the limiting conditions of a *thermodynamically reversible* change, which for an electrochemical cell implies zero current. The more rapidly the cell operates, the less electrical work it can supply.
- If F is expressed in coulombs per mole of electrons, the electrical work is in joules per mole. To relate these units to electrical units, recall that the coulomb is one amp-sec, and that *power*, which is the rate at which work is done, is measured in watts, which is the product of amps and volts

$$1 \text{ J} = 1 \text{ watt-sec} = 1 \text{ (amp-sec)} \times \text{volts}$$

Thus the *volt* has the dimensions of joules/coulomb— the energy produced per quantity of charge passing through the cell. Because voltage is the quotient of two extensive quantities, it is itself *intensive*. When we multiply the anodic and cathodic half-reactions by the stoichiometric factors required to ensure that each involves the same quantity of charge, the free energy change and the number of coulombs both increase by the same factor, leaving the potential (voltage) unchanged. This explains why we do not have to multiply the E° 's of the anode and cathode reactions by stoichiometric factors when we are finding the potential of a complete cell.

If Eq. 2 is solved for E° , we have

$$E^\circ = \frac{\Delta G^\circ}{nF} \quad (16.3.10)$$

This states explicitly that the cell potential is a measure of the free energy change *per mole of electrons transferred*, which is a brief re-statement of the principle explained immediately above. To see this more clearly, consider the cell



for which we list the standard reduction potentials and ΔG° 's of the half-reactions:

reaction	E°	$-nFE^\circ = \Delta G^\circ$
cathode: $2 \times [\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-]$	+0.222 v	-42800 J
anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2 e^-$	-(+.337) V	+65000 J
net: $2 \text{Ag(s)} + 2 \text{Cl}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{AgCl(s)} + \text{Cu(s)}$		
cell: $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{AgCl(s)} \mid \text{Cl}^-(\text{aq}) \mid \text{Ag(s)}$	-0.115 v	+22200 J

Here we multiply the cathodic reaction by two in order to balance the charge. Because the anodic reaction is written as an oxidation, we reverse the sign of its E° and obtain $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.115$ volt for the cell potential. The negative cell potential tells us that this reaction will not proceed spontaneously.

When the electrons don't cancel out

Note, however, that if we are combining two half reactions to obtain a third half reaction, the E° values are not additive, since this third half-reaction is not accompanied by another half reaction that causes the charges to cancel. Free energies are always additive, so we combine them, and use $\Delta G^\circ = -nFE^\circ$ to find the cell potential.

✓ Example 16.3.2

Calculate E° for the electrode $\text{Fe}^{3+}/\text{Fe(s)}$ from the standard potential of the couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{2+}/\text{Fe(s)}$

Solution

Tabulate the values and calculate the ΔG° 's as follows:

(i) $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	$E^\circ_1 = .771 \text{ v}, \Delta G^\circ_1 = -.771 F$
(ii) $\text{Fe}^{2+} + 2 e^- \rightarrow \text{Fe(s)}$	$E^\circ_2 = -.440 \text{ v}, \Delta G^\circ_2 = +.880 F$
(iii) $\text{Fe}^{3+} + 3 e^- \rightarrow \text{Fe(s)}$	$E^\circ_3 = ?, \Delta G^\circ_3 = +.109 F$

The Gibbs energy for half-reaction (iii) is $0.109nF$, so $E^\circ_3 = -.109/3 = -.036 \text{ v}$

The fall of the electron

A table of standard half-cell potentials summarizes a large amount of chemistry, for it expresses the relative powers of various substances to donate and accept electrons by listing reduction half-reactions in order of increasing E° values, and thus of increasing spontaneity. The greater the value of E° , the greater the tendency of the substance on the left to acquire electrons, and thus the stronger this substance is as an oxidizing agent.

If you have studied elementary chemical thermodynamics, you will have learned about the role that a quantity called the *Gibbs free energy*, usually referred to as simply the "free energy", plays in determining the direction of any chemical change. The rule is that all spontaneous change (that is, all reactions that proceed to the "right") is associated with a fall in the free energy, and the greater the degree of that fall (ΔG°), the greater will be the tendency for the reaction to take place.

If you are not familiar with the concept of free energy, just think of it as something like potential energy, which similarly decreases when spontaneous mechanical events occur, such as the dropping of a weight.

Since oxidation-reduction processes involve the transfer of an electron from a donor to an acceptor, it makes sense to focus on the electron and to consider that it falls from a higher-free energy environment (the reductant, or "source") to a lower-free energy one (the oxidant, or "sink".)

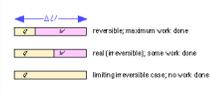
As can be seen from the diagram below, this model makes it far easier to predict what will happen when two or more oxidants and reductants are combined; the electron "falls" as far as it can, filling up oxidizing agents (sinks) from the bottom up, very much in the same way as electrons fill atomic orbitals as we build up larger atoms.

Electron-free energy diagram of redox couples

This chart is essentially an abbreviated form of a table of standard potentials in which the various couples are displayed on a vertical scale corresponding to $E^\circ = -\Delta G^\circ/nF$. Any available sink on the right side will tend to drain electrons from a source above it. For example, immersion of metallic zinc in a solution of CuSO_4 will result in the reduction of Cu^{2+} to metallic copper (red arrows.) Similarly, addition of chlorine to water will tend to oxidize the water, producing O_2 and Cl^- (blue arrows.) Note especially the positions of the H_2/H^+ and $\text{H}_2\text{O}/\text{O}_2, \text{H}^+$ couples on this chart, as they define the range of E° 's for substances that will not decompose water (green region.)

A more detailed table with a more complete explanation can be seen on the "[Fall of the electron](#)" tutorial page; it is strongly recommended that you take the time to acquire a thorough understanding of this concept.

At this point, it might be worth calling your attention to the similar way of depicting acid-base reactions as representing the "fall of the proton" as shown below and described much more thoroughly [here](#).



Proton-free energy diagram of acid-base systems

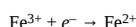
Acids are *proton sources* (donors), bases are *proton sinks*. Protons "fall" (in free energy) whenever a base is present that presents proton-empty free energy levels. The red arrows show what happens when acetic acid is titrated with a strong base; the results are acetate ion and water. Note here again the crucial role of water, both as a proton acceptor (forming hydronium ion) and as a proton donor (forming hydroxide ion.) Note also that the pH of a solution is a direct measure of the average free energy of protons in the solution (relative to H_3O^+ .)

An important difference between proton transfer and electron transfer reactions is that the latter can vary greatly in speed, from almost instantaneous to so slow as to be unobservable. Acid-base reactions are among the fastest known.

Considerable insight into the chemistry of a single element can be had by comparing the standard electrode potentials (and thus the relative free energies) of the various oxidation states of the element. The most convenient means of doing this is the *Latimer diagram*. As examples, diagrams for iron and chlorine are shown below.

The formulas of the species that represent each oxidation state of the element are written from left to right in order of decreasing oxidation number, and the standard potential for the reduction of each species to the next on the right is written in between the formulas. Potentials for reactions involving hydrogen ions will be pH dependent, so separate diagrams are usually provided for acidic and alkaline solutions (effective hydrogen ion concentrations of 1M and 10^{-14} M, respectively).

The more positive the reduction potential, the greater will be the tendency of the species on the left to be reduced to the one on the right. To see how Latimer diagrams are used, look first at the one for iron in acid solution. The line connecting Fe^{3+} and Fe^{2+} represents the reaction



whose positive E° (.440 v) indicates that metallic iron will dissolve in acidic solution to form Fe^{2+} . Because the oxidation of this species to the +3 state has a negative potential (-0.771v; moving to the left on the diagram reverses the sign), the +2 state will be the stable oxidation state of iron under these conditions.

Disproportionation

An important condition to recognize in a Latimer diagram is when the potential on the left of a species is less positive than that on the right. This indicates that the species can oxidize and reduce itself, a process known as *disproportionation*. As an example, consider Cl_2 in alkaline solution. The potential for its reduction to Cl^- is sufficiently positive (+1.35 v) to supply the free energy necessary for the oxidation of one atom of chlorine to hypochlorite. Thus elemental chlorine is thermodynamically unstable with respect to disproportionation in alkaline solution, and the same is true of the oxidation product, ClO^- (hypochlorite ion).



Behavior of chlorine in water

Cl_2 can oxidize water (green arrows, top) and also undergo disproportionation (purple arrows, bottom). In the latter process, one Cl_2 molecule donates electrons to another. Bear in mind that many oxidation-reduction reactions, unlike most acid-base reactions, tend to be very slow, so the fact that a species is thermodynamically unstable does not always mean that it will quickly decompose. Thus the two reactions shown in the figure are normally very slow.

Thermodynamics of Galvanic cells

The free energy change for a process represents the maximum amount of non-PV work that can be extracted from it. In the case of an electrochemical cell, this work is due to the flow of electrons through the potential difference between the two electrodes. Note, however, that as the rate of electron flow (i.e., the current) increases, the potential difference must decrease; if we short-circuit the cell by connecting the two electrodes with a conductor having negligible resistance, the potential difference is zero and no work will be done. The full amount of work can be realized only if the cell operates at an infinitesimal rate; that is, reversibly.

You should recall that this is exactly analogous to the expansion of an ideal gas. The full amount of work $w = PdV$ is extracted only under the special condition that the external pressure P opposing expansion is only infinitesimally smaller than the pressure of the gas itself. If the gas is allowed to expand into a vacuum ($P = 0$), no work will be done.

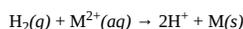


The total amount of energy a reaction can supply under standard conditions at constant pressure and temperature is given by ΔH° . If the reaction takes place by combining the reactants directly (no cell) or in a short-circuited cell, no work is done and the heat released is ΔH . If the reaction takes place in a cell that performs electrical work, then the heat released is diminished by the amount of electrical work done. In the limit of reversible operation, the heat released becomes

$$\Delta H = \Delta G^\circ + T \Delta S$$



whose left half consists of a *standard hydrogen electrode* (SHE) and whose net reaction is



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